



ISSN 1001-0742
CN 11-2629/X

2012

Volume **24**
Number **7**

JOURNAL OF
**ENVIRONMENTAL
SCIENCES**



Sponsored by
Research Center for Eco-Environmental Sciences
Chinese Academy of Sciences

JOURNAL OF ENVIRONMENTAL SCIENCES

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CONTENTS

Aquatic environment

Investigation of the hydrodynamic behavior of diatom aggregates using particle image velocimetry Feng Xiao, Xiaoyan Li, Kitming Lam, Dongsheng Wang.....	1157
Shellac-coated iron oxide nanoparticles for removal of cadmium(II) ions from aqueous solution Jilai Gong, Long Chen, Guangming Zeng, Fei Long, Jiuhua Deng, Qiuya Niu, Xun He.....	1165
Prediction of DOM removal of low specific UV absorbance surface waters using HPSEC combined with peak fitting Linan Xing, Rolando Fabris, Christopher W. K. Chow, John van Leeuwen, Mary Drikas, Dongsheng Wang.....	1174
Photo-production of dissolved inorganic carbon from dissolved organic matter in contrasting coastal waters in the southwestern Taiwan Strait, China Weidong Guo, Liyang Yang, Xiangxiang Yu, Weidong Zhai, Huasheng Hong.....	1181
One century sedimentary record of lead and zinc pollution in Yangzong Lake, a highland lake in southwestern China Enlou Zhang, Enfeng Liu, Ji Shen, Yanmin Cao, Yanling Li.....	1189
Antimony(V) removal from water by iron-zirconium bimetal oxide: Performance and mechanism Xuehua Li, Xiaomin Dou, Junqing Li.....	1197
Carbonaceous and nitrogenous disinfection by-product formation in the surface and ground water treatment plants using Yellow River as water source Yukun Hou, Wenhai Chu, Meng Ma.....	1204
Water quality evaluation based on improved fuzzy matter-element method Dongjun Liu, Zhihong Zou.....	1210
Formation and cytotoxicity of a new disinfection by-product (DBP) phenazine by chloramination of water containing diphenylamine Wenjun Zhou, Linjie Lou, Lifang Zhu, Zhimin Li, Lizhong Zhu.....	1217

Atmospheric environment

Chemical compositions of PM _{2.5} aerosol during haze periods in the mountainous city of Yong'an, China Liqian Yin, Zhenchuan Niu, Xiaoqiu Chen, Jinsheng Chen, Lingling Xu, Fuwang Zhang.....	1225
Decomposition of trifluoromethane in a dielectric barrier discharge non-thermal plasma reactor M. Sanjeeva Gandhi, Y. S. Mok.....	1234
Transverse approach between real world concentrations of SO ₂ , NO ₂ , BTEX, aldehyde emissions and corrosion in the Grand Mare tunnel I. Ameur-Bouddabbous, J. Kasperek, A. Barbier, F. Harel, B. Hannoyer.....	1240
A land use regression model incorporating data on industrial point source pollution Li Chen, Yuming Wang, Peiwu Li, Yaqin Ji, Shaofei Kong, Zhiyong Li, Zhipeng Bai.....	1251

Terrestrial environment

Effect of vegetation of transgenic Bt rice lines and their straw amendment on soil enzymes, respiration, functional diversity and community structure of soil microorganisms under field conditions Hua Fang, Bin Dong, Hu Yan, Feifan Tang, Baichuan Wang, Yunlong Yu.....	1259
Enhanced flushing of polychlorinated biphenyls contaminated sands using surfactant foam: Effect of partition coefficient and sweep efficiency Hao Wang, Jiajun Chen.....	1270
Transpiration rates of urban trees, <i>Aesculus chinensis</i> Hua Wang, Xiaoke Wang, Ping Zhao, Hua Zheng, Yufen Ren, Fuyuan Gao, Zhiyun Ouyang.....	1278

Environmental biology

Methanogenic community dynamics in anaerobic co-digestion of fruit and vegetable waste and food waste Jia Lin, Jiane Zuo, Ruofan Ji, Xiaojie Chen, Fenglin Liu, Kaijun Wang, Yunfeng Yang.....	1288
Differential fate of metabolism of a disperse dye by microorganisms <i>Galactomyces geotrichum</i> and <i>Brevibacillus laterosporus</i> and their consortium GG-BL Tatoba R. Waghmode, Mayur B. Kurade, Anuradha N. Kagalkar, Sanjay P. Govindwar.....	1295

Environmental catalysis and materials

Effects of WO _x modification on the activity, adsorption and redox properties of CeO ₂ catalyst for NO _x reduction with ammonia Ziran Ma, Duan Weng, Xiaodong Wu, Zhichun Si.....	1305
Photocatalytic degradation of bisphenol A using an integrated system of a new gas-liquid-solid circulating fluidized bed reactor and micrometer Gd-doped TiO ₂ particles Zhiliang Cheng, Xuejun Quan, Jinxin Xiang, Yuming Huang, Yunlan Xu.....	1317
Effect of CeO ₂ and Al ₂ O ₃ on the activity of Pd/Co ₃ O ₄ /cordierite catalyst in the three-way catalysis reactions (CO/NO/C _n H _m) Sergiy O. Soloviev, Pavlo I. Kyriienko, Nataliia O. Popovych.....	1327

Environmental analytical methods

Development of indirect competitive fluorescence immunoassay for 2,2',4,4'-tetrabromodiphenyl ether using DNA/dye conjugate as antibody multiple labels Zi-Yan Fan, Young Soo Keum, Qing-Xiao Li, Weilin L. Shelver, Liang-Hong Guo.....	1334
A novel colorimetric method for field arsenic speciation analysis Shan Hu, Jinsuo Lu, Chuanyong Jing.....	1341
Aminobenzenesulfonamide functionalized SBA-15 nanoporous molecular sieve: A new and promising adsorbent for preconcentration of lead and copper ions Leila Hajiaghatabaei, Babak Ghasemi, Alireza Badieli, Hassan Goldooz, Mohammad Reza Ganjali, Ghodsi Mohammadi Ziarani.....	1347



One century sedimentary record of lead and zinc pollution in Yangzong Lake, a highland lake in southwestern China

Enlou Zhang, Enfeng Liu, Ji Shen*, Yanmin Cao, Yanling Li

State Key Laboratory of Lake Science and Environment, Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences, Nanjing 210008, China. E-mail: jishen@niglas.ac.cn

Received 17 August 2011; revised 26 December 2011; accepted 31 December 2011

Abstract

Reconstruction of trace metal pollution histories and sources may help us to regulate current pollutant discharge. This is especially important for the highland lakes in southwestern China, which are facing trace metals pollution. We present sedimentary records of 11 metals accumulated in Yangzong Lake since the 1870's, a highland lake in southwestern China. Pollution of lead and zinc (Pb and Zn) was differentiated based on principal component analysis, geochemical normalization, and lead isotope ratios. Nearly all the metals as well as grain size composition show generally constant values before the mid-1980's, denoting stable detrital input in the catchment. Fluctuations in the concentrations of the metals as well as grain size composition since the mid-1980's indicate an increase in soil erosion with strengthened human disturbance in the catchment. After geochemical normalization, Pb and Zn showed constant values before 1990 AD and then a gradual increase in parallel with the variations in $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios, indicating that Pb and Zn pollution occurred. Combining the data of $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios in the sediments of Yangzong Lake, leaded gasoline, Pb-Zn ore and coal, and consumption or production historical trends, we deduced that the enhanced Pb and Zn pollution in Yangzong Lake is caused primarily by ore mining and refining.

Key words: Pb, Zn; pollution; temporal trend; sediment; Yangzong Lake

DOI: 10.1016/S1001-0742(11)60896-6

Introduction

Human activities have been causing dramatic increases in the load of trace metals to the environment, particularly during the industrial period (Nriagu, 1996). Lake sediments are one of the main pollutant pools and can provide useful spatial and temporal information on trace metal pollution related to anthropogenic input from atmospheric deposition of local or remote sources, as well as the river input of the local industrial sources (Yang and Rose, 2003, 2005; Wu et al., 2010). The commonly observed trace metal pollution in Europe began in the early 1800s and experienced a sharp increase in the 1900's with the steady increase in industrialization and the usage of leaded gasoline, followed by decrease in past decades with the implementation of environmental protection measures such as the prohibition of lead as a gasoline additive (Yang and Rose, 2003, 2005; Nriagu, 1996). In contrast with the developed countries, trace metal pollution has shown increasing trends recently in developing countries, including China (Rose et al., 2004; Chen et al., 2005; Wang et al., 2006, 2010; Shi et al., 2010; Wu et al., 2010). Although trace metal pollution has been extensively studied in the eastern coastal/industrial regions of China

(Rose et al., 2004; Chen et al., 2005; Wang et al., 2006; Wu et al., 2010; Shi et al., 2010), little is known about the trace metal pollution in the west and southwest highland areas of China. Recent research also indicates that the highland lakes of the Tibetan Plateau, which were usually considered to be in a pristine state, also suffered from trace metal pollution, generally since the implementation of the "Reform and Open" policy in the late-1970s (Loewen et al., 2007; Wang et al., 2010). The highland region in southwestern China, which is adjacent to the Tibetan Plateau, is one of the centers of non-ferrous ore mining and smelting. The non-ferrous metal production in Yunnan Province increased to about 1.5×10^5 tons annually by the mid-1980's from less than 1×10^4 tons in the early 1950's, and then reached over 2.0×10^6 tons in recent years. Less well-controlled smelting emissions and increasing consumption of coal caused southwestern China to experience serious trace metal (Hg, Pb, Cd, Zn etc.) pollution currently (Bi et al., 2006; Li et al., 2008). However, the temporal trend of the trace metal pollution and atmospheric contribution to the aquatic system was seldom studied (Zeng and Wu, 2009; Zhao et al., 2011).

Yangzong Lake is situated in the central Yunnan-Guizhou Plateau. After arsenic pollution occurred in 2008 due to wastewater discharge, it has received much attention

* Corresponding author. E-mail: jishen@niglas.ac.cn

focused on trace metal pollution. Pb and Zn are two typical trace metals accompanying the steady increase in industrialization. Potential sources, including Pb-Zn ore mining and refining, coal consumption, and usage of leaded gasoline may all contribute to the Pb and Zn pollution in Yangzong Lake especially during recent decades with the onset of rapid economic development. The aims of the present study are to reveal the historical character of Pb and Zn accumulation in the sediments of Yangzong Lake, and to uncover the pollution trends and potential anthropogenic sources.

1 Site description

Yangzong Lake (24°51'N to 24°58'N, 102°58'E to 103°01'E) is located in Yiliang County, Yunnan Province, southwestern China (Fig. 1). The lake is located at 1770.7 m above sea level, and covers an area of 31 km², with an average water depth 20 m (Wang and Dou, 1998). Yangzong Lake is recharged by precipitation and runoff from the rivers distributed in the south and north of the catchment, and some temporal streams (Fig. 1). The water is discharged into the Nanpan River through the Baiyi River in the northeast of the catchment (Wang and Dou, 1998). Annual precipitation in the watershed is 825 mm, of which 85% occurs during May–October (Wang and Dou, 1998).

The lake is surrounded by mountains, with the highest altitude 2730 m. The catchment area is 192 km². In

2004, land cover included agricultural pastures (35.7%), forest (23.7%), grassland (18.0%), lakes/rivers (16.3%), and residential/industrial zones (6.3%) (Zhu, 2008). Due to the low forest cover, high gradient and intensive human activities, about 65% of the catchment area is suffering from the influence of soil loss (Zhu, 2008). Rapid economic development has placed great pressure on the ecological environment of Yangzong Lake. Water quality has deteriorated in recent decades (Zhu, 2008). The lake is also suffering from the influence of acid precipitation (Zhu et al., 2002; Wang et al., 2005).

2 Material and methods

In 2007, one 44 cm long sediment core was collected from the deepest part of Yangzong Lake using a gravity corer. The core sediment had a clear water-sediment interface, which denoted that the occurrence of disturbance was absent during the sampling. Referencing to the previous palaeolimnology work (Davis et al., 2006; Dearing et al., 2006; Balogh et al., 2010), the core used in our study should record the environment change of terrestrial input and atmospheric deposition. The core was sampled at 0.5 cm resolution and then the samples were stored in an incubator chilled with ice bags in the field and stored at 4°C in the laboratory before analysis.

Both ¹³⁷Cs ($T_{1/2} = 30.1$ yr) and ²¹⁰Pb ($T_{1/2} = 22.3$ yr) dating methods were used to establish the chronology of the sediment core (Appleby, 2001). ¹³⁷Cs, ²¹⁰Pb and ²²⁶Ra activities of the samples were measured using an Ortec HPGGe GWL series well-type coaxial low background intrinsic germanium detector (GWL120-15, AMETEK, USA). ¹³⁷Cs was measured by its emissions at 662 keV. ²¹⁰Pb was determined via its gamma emissions at 46.5 keV, ²²⁶Ra by the 295 and 352 keV gamma rays emitted by its daughter isotope ²¹⁴Pb following 3 weeks of storage in sealed containers to allow radioactive equilibrium to be reached. The activities of excess ²¹⁰Pb (²¹⁰Pb_{ex}) in each sample were obtained by subtracting ²²⁶Ra activities from activities of total ²¹⁰Pb (Fig. 2), and used for the chronology calculation.

Concentrations of spheroidal carbonaceous particles (SCPs) in the sediment core were determined following the procedure introduced by Rose (1994). SCPs are produced from the high temperature combustion of fossil-fuels and have no natural sources. Therefore, the appearance of SCPs in the sediment and their concentration variation provides an unambiguous record of industrial development stages, which can be used for sediment dating (Rose et al., 2004).

Freeze-dried and ground samples (0.125 g) were totally digested with HNO₃-HCl-HF (US EPA, 1996), and prepared for the determination of elements (Al, Fe, Na, K, Ca, Ti, Mg, Li, Pb and Zn) by inductively coupled plasma atomic emission spectrometry (ICP-AES, Profile DV, Teledyne Leeman Labs, USA). Data quality was ensured through the use of duplicates, blanks, and standard reference material GSD-11 supplied by the Chinese Academy of Geological Sciences. The standard deviations for determined values of the metals in GSD-11 were < 7%

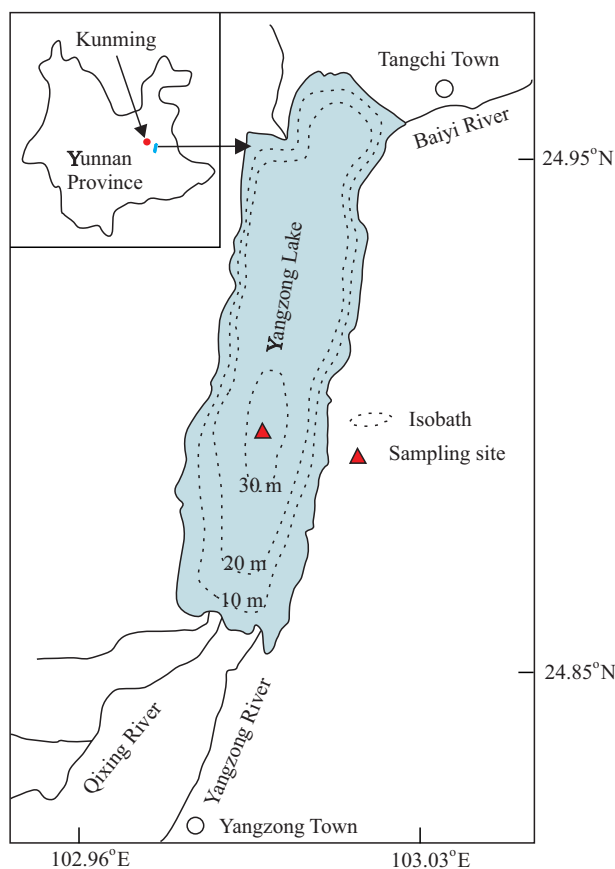


Fig. 1 Maps showing the location of Yangzong Lake, Yunnan Province, China and sampling site of the sediment core.

of the certified values.

Lead isotopes (^{208}Pb , ^{207}Pb and ^{206}Pb) of the selected samples after $\text{HNO}_3\text{-HCl-HF}$ digestion were determined by inductively coupled plasma mass spectroscopy (ICP-MS, 7700x, Agilent, USA). An international standard reference material (SRM981-NIST) was used for calibration and analytical control. The maximum relative standard deviations of measured $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ for standard reference material GBW04426 were $< 0.15\%$.

The variations in lithogenic input complicate the differentiation of trace metal pollution from the lake sedimentary records. Thus, the methods of principal component analysis (PCA) were employed to check for geochemical associations and to ascertain the factors that control the origin of the metals, which were conducted using SPSS 12.0 for Windows.

To remove artifacts in the trace metal concentrations due to changes in sediment texture, a geochemical normalization technique is introduced in this work (Aloupi and Angelidis, 2001; Matthai and Birch, 2001). Normalized concentrations (M_{nor}) of Pb and Zn were calculated by:

$$M_{\text{nor}} = \frac{M_{\text{con}}}{(X_{\text{con}}/X_{\text{ave}})}$$

where, M is the evaluated element, X is the normalizer, and M_{con} is the concentration of evaluated element in each sample. $X_{\text{con}}/X_{\text{ave}}$ is the concentration of the normalizer in each sample rescaled to the average values.

3 Results

3.1 Chronology

As shown in Fig. 2, a large, broad peak in ^{137}Cs roughly peaking at 18-cm depth corresponds to the 1963–1964 AD

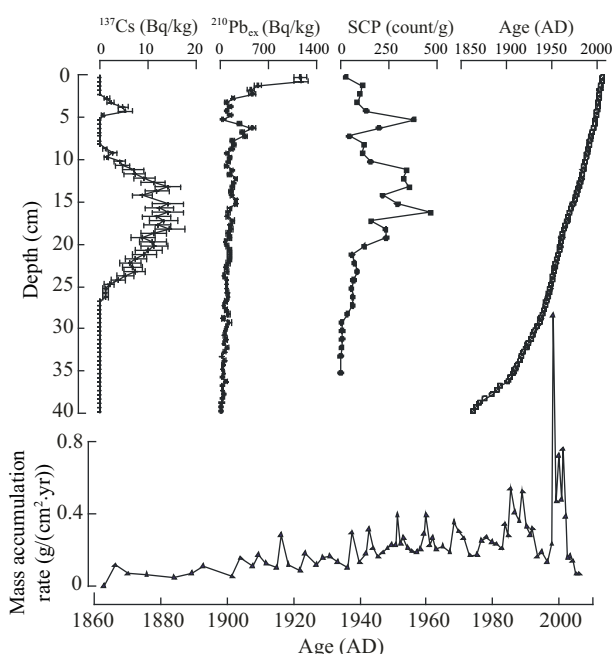


Fig. 2 Activities of ^{137}Cs and $^{210}\text{Pb}_{\text{ex}}$, SCP concentrations, mass accumulation rates and age depth curves for the Yangzong Lake sediment core.

maximum fallout from atmospheric nuclear bomb testing (Appleby, 2001). $^{210}\text{Pb}_{\text{ex}}$ shows a logarithmic decrease with depth with extensive variations (Fig. 2), which may be the result of changes in terrestrial material supplementation and fluctuation in accumulation rates. Therefore, a constant rate of supply (CRS) dating model was used for the chronology calculation (Appleby, 2001). The ^{137}Cs date of 1963 AD was used for minor correction of the ^{210}Pb -based chronology following the procedure described by Appleby (2001). The calculated chronology and mass accumulation rate over the last 140 years are presented in Fig. 2. The mass accumulation rates increased gradually and exhibited peak values during 1985–1992 AD and 1998–2002 AD.

Concentrations of SCPs increased upwards from 0 below 32.5 cm, and kept at relatively low values up to 21 cm, followed thereafter by a marked increase upwards (Fig. 2). The concentration showed notably lower values in the range 10.5–6.5 cm and decreased in the upper 5–0 cm. Since SCPs are produced from high temperature combustion of fossil-fuels (mainly coal) (Rose, 1994), the Yangzong power plant may be the main supplier, as one of the largest fuel-burning power plants in Kunming area. Due to the lack of coal consumption data, the method of comparison between SCPs and the coal consumption (Yang and Rose, 2003, 2005; Rose et al., 2004; Wu et al., 2010) may not be useful in this study. However, there is strong evidence that the SCPs concentrations increased at around 1960 AD (at 20.5 cm), which matches the time (1959 AD) when the power plant was built and started to run. Therefore, we deduce that the chronology of the sediment constructed based on the ^{137}Cs and ^{210}Pb dating methods is reasonable.

3.2 Grain size

Sediments in Yangzong Lake are mainly composed of fine-grained ($< 16 \mu\text{m}$) material, which account for 56%–96% of the grain composition, with an average of 87% (Fig. 3). Clay ($< 4 \mu\text{m}$) and fine silt ($4\text{--}16 \mu\text{m}$) showed similar variations with depth, but they varied in an opposite sense to the coarse silt ($16\text{--}63 \mu\text{m}$) and sand ($> 63 \mu\text{m}$) fractions. Temporally, the sediment displayed generally constant grain size composition before the mid-1980's, followed by extensive fluctuations. Generally coarser grain size compositions were dominant during 1985–1992 AD and 1998–2002 AD.

3.3 Vertical variations of metals

Vertical variations of the metals are shown in Fig. 3. Constant values of the metals were observed before the mid-1940's followed by a slight decrease except for Ca, and then constant values were maintained till the mid-1980's. After that, the metals showed large fluctuations. Extraordinarily higher values for Mg, K and Li were displayed during 1985–1992 AD and for Al, Fe, Na, Mg, K, Ti and Li during 1998–2002 AD, when mass accumulation rates were high (Fig. 2). It can be found that variations of the metal concentrations were all accompanied by variations in the grain size composition.

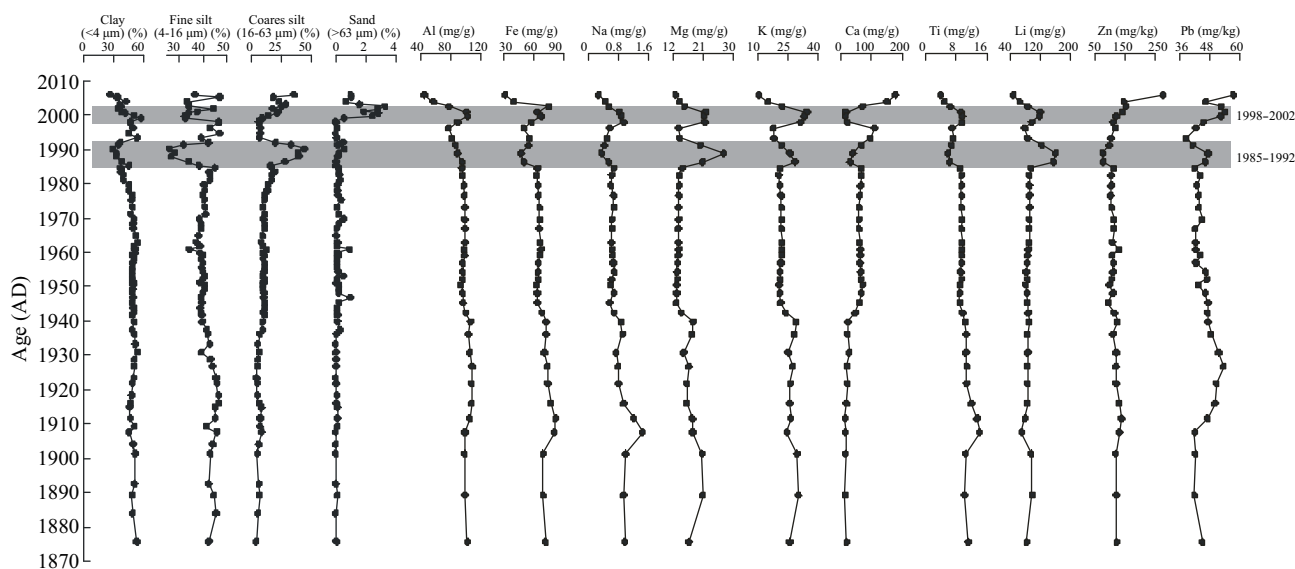


Fig. 3 Diagram of grain size composition, and concentrations of the major and trace metals in the sediment core.

3.4 Principal component analysis (PCA)

Principal component analysis (PCA) was performed to determine the geochemical associations between the metals and to ascertain the source information (Selvaraj et al., 2010). The fine-grained fraction ($< 16 \mu\text{m}$) content has been included as it plays a key role in the enrichment of metals in sediments (Chen et al., 2004; Zhang et al., 2002). The rotation of principal components was carried out by the Varimax normalized method and only the variables that show loadings > 0.5 were considered for provenance interpretation.

Three principal components (PC) were identified with eigenvalues higher than 1, which account for 88.594% of the total variance in the data matrix (Table 1). PC1 accounts for 49.085% of the total variance, and explained the cumulative variances involving Al, Fe, Na, Ti, Ca, K and fine-grained fractions. PC2 is dominated by Mg, K, and Li, accounting for 24.361% of the total variance. PC3 accounts for 15.148% of the total variance, and explained the cumulative variances of Pb and Zn. As typical lithogenic elements, Al, Na, K and Ti are considered to be one of the most reliable terrigenous erosion indicators of rocks and soil parent material, which are scarcely enriched by human contamination (Chen et al., 2004; Rose et al., 2004; Shi et al., 2010; Selvaraj et al., 2010). Therefore, PC1 and PC2 indicate the dominating natural input. Pb and Zn are positively correlated ($r = 0.544$, $p < 0.01$), however, they have weak or absent correlations with the metals in PC1 and PC2 (Table 2), which denote anthropogenic sources besides the detrital origins for Pb and Zn.

3.5 Geochemical normalization of trace metals

The synchronous variations of the metals and grain size composition indicated that concentrations of the metals were influenced by the lithogenic input (Zhang et al., 2002; Chen et al., 2004; Aloupi and Angelidis, 2001; Matthai and Birch, 2001). The geochemical normalization technique allows the removal of artifacts in the metal concentrations due to changes in sediment texture and

the differentiation of anthropogenic contribution to the enrichment of Pb and Zn from natural origins (Aloupi and Angelidis, 2001; Matthai and Birch, 2001; Chen et al., 2004; Rose et al., 2004). Al, Fe, Li, Ti, Co, and Cs have often been used as normalizers (Aloupi and Angelidis, 2001; Matthai and Birch, 2001; Rose et al., 2004; Chen et al., 2004; Reimann and de Caritat, 2005). However, the choice of a normalizer is not universal and depends on geological and physicochemical characteristics of the study area (Reimann and de Caritat, 2005). Single-element normalization was generally used in previous research (Aloupi and Angelidis, 2001; Matthai and Birch, 2001; Rose et al., 2004; Chen et al., 2004; Reimann and de Caritat, 2005), which may be insufficient to compensate for sediment texture variations. Here, Al, Li and Ti are used as the normalizer for Pb and Zn to check the effectiveness of geochemical normalization. Normalized concentrations of Pb and Zn are shown in Fig. 4. Pb and Zn show similar variations along the depth after the normalization by Al, Li and Ti. Values of Pb and Zn normalized by the elements Al, Ti and Li all increase sharply since 2000 AD. However, more stable variations of Pb/Al and Zn/Al in the sediment

Table 1 Principal components (PC) analysis of the metals in the core sediments of Yangzong Lake

Parameter	Rotated component matrix		
	PC1	PC2	PC3
Al	0.816	0.327	-0.321
Fe	0.922	0.038	-0.058
Na	0.895	0.081	0.148
Ti	0.972	-0.001	-0.056
Ca	-0.775	-0.615	0.091
K	0.570	0.773	0.072
Mg	0.033	0.915	0.126
Li	-0.213	0.901	-0.331
Pb	-0.017	0.190	0.847
Zn	-0.194	-0.361	0.862
Fine-grained fraction	0.816	0.327	-0.321
Initial eigenvalues	5.399	2.680	1.666
Variance	49.085%	24.361%	15.148%
Cumulative	49.085%	73.446%	88.594%

Table 2 Correlation coefficient of the metals and grain size fractions in the core sediments of Yangzong Lake

	Al	Fe	Na	Mg	K	Ca	Ti	Li	Zn	Pb	Clay	Fine silt	Coarse silt
Fe	0.821**												
Na	0.593**	0.750**											
Mg	0.175	0.002	0.235										
K	0.671**	0.509**	0.587**	0.739**									
Ca	-0.871**	-0.755**	-0.711**	-0.568**	-0.903**								
Ti	0.815**	0.895**	0.888**	0.041	0.510**	-0.755**							
Li	0.269	-0.123	-0.194	0.728**	0.534**	-0.423**	-0.184						
Zn	-0.579**	-0.257	-0.030	-0.178	-0.319	0.451**	-0.217	-0.568**					
Pb	-0.098	-0.017	-0.031	0.131	0.182	-0.038	-0.098	-0.070	0.544**				
Clay (< 4 μm)	0.569**	0.552**	0.437**	-0.297	0.210	-0.359*	0.578**	-0.280	-0.378*	-0.296			
Fine silt (4–16 μm)	0.382*	0.514**	0.669**	-0.198	0.156	-0.337*	0.674**	-0.480	0.013	-0.119	0.377*		
Coarse silt (16–63 μm)	-0.588**	-0.661**	-0.644**	0.308	-0.241	0.424**	-0.739**	0.440**	0.242	0.237	-0.899**	-0.740**	
Sand (>63 μm)	-0.272	-0.029	-0.156	0.127	0.111	0.112	-0.297	0.076	0.377*	0.500**	-0.327*	-0.469**	0.395*

** Correlation is significant at the 0.01 level and 0.05 level (2-tailed), respectively.

before 1990 AD can be observed compared to the values of Pb/Ti, Pb/Li, Zn/Ti, and Zn/Li. This may imply that geochemical normalization using Al as the normalizer is more appropriate than Li and Ti. Therefore, Pb/Al and Zn/Al are referenced for the pollution evaluation. In view of the undeveloped industry in southwestern China before the 1950's, the relatively low and constant normalized values for Pb and Zn in the lower part of the sediment core may be the background values before the industrial era, while the increased values since around 2000 AD imply the presence of anthropogenic input.

3.6 Lead isotopes in core sediments

$^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ present small variation ranges (1.994–2.074 and 0.800–0.841, respectively) in the sediments of Yangzong Lake (Fig. 4). The vertical variations of $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios are similar to those of Pb/Al and Zn/Al, but the transition to increasing values for $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios appears earlier than that of Pb/Al and Zn/Al, which is around 1990 AD (Fig. 4).

4 Discussion

Trace metals in the aquatic environment can originate from the natural processes of weathering, erosion, and transport

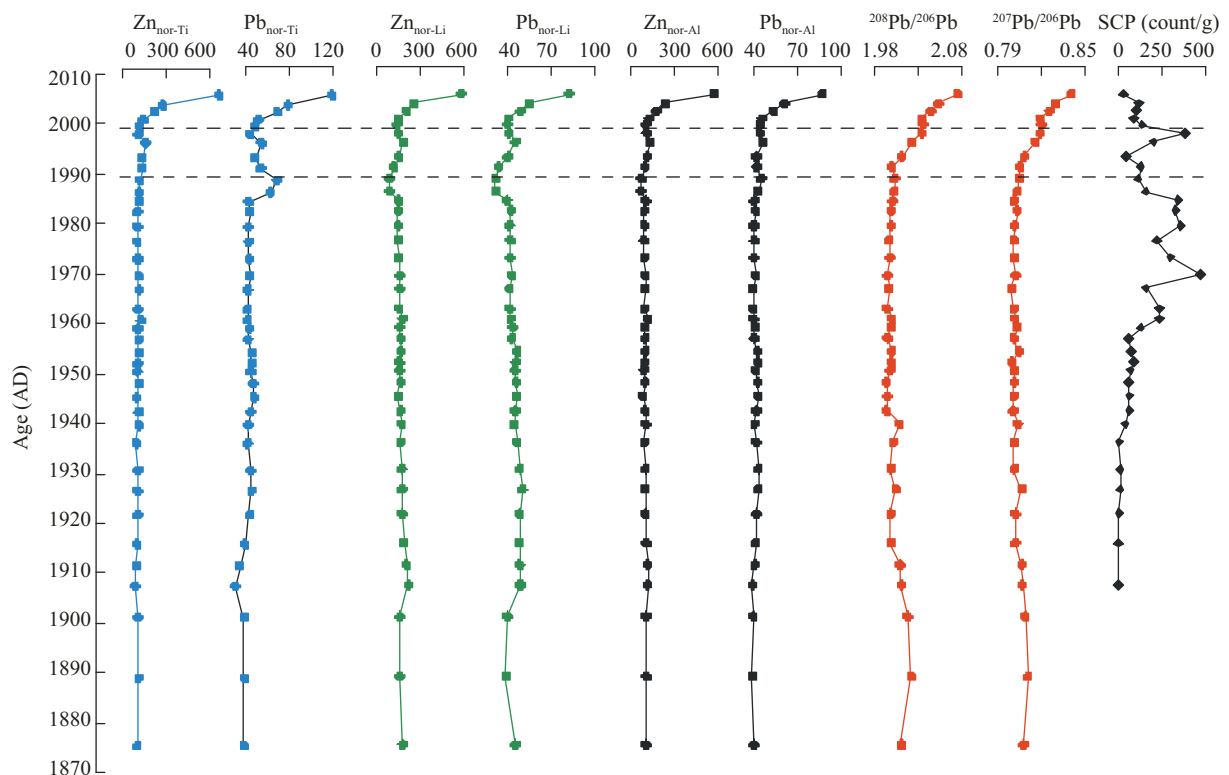


Fig. 4 Normalized concentrations of Zn and Pb, lead isotopes and SCPs in the Yangzong Lake sediment core.

of bedrock and soils, as well as from anthropogenic sources, such as wastewater discharge, and depositions of aerosols resulting from vehicle emissions and industrial sources (e.g., ore mining and refining, coal burning). Major metals in sediments are predominantly sourced from the natural processes of weathering, erosion and transport of bedrock and soils (Yang et al., 2004), and were used in the present work to illustrate the supply of detrital materials and the driving mechanisms, combined with the grain size composition.

The parameters of major metals and grain size composition showed generally constant values prior to the mid-1980's, implying stable detrital input related to lower human perturbation in the watershed of Yangzong Lake (Davis et al., 2006; Dearing et al., 2006). Variations in major metals and grain size composition in Yangzong Lake during 1985–1992 AD and 1998–2002 AD were accompanied by higher sedimentary rates. This was related to the changed terrestrial materials supply, and acceleration of erosion by changed precipitation or human perturbation on the landform of the watershed (Tylmann, 2005; Davis et al., 2006; Dearing et al., 2006). Nevertheless, there have been no substantial changes in the precipitation in recent decades in the Yangzong Lake area (<http://cdc.cma.gov.cn/shuju/index.jsp?current=2&tpcat=SURF>), suggesting that the variation is not caused by flooding events. Moreover, reclamation was enhanced during the 1980's and some terraces were built in the Yangzong Lake catchment (Zhu, 2008). It is well known that reclamation is usually accompanied by enhanced erosion and thus more coarse-grained material could be introduced into the lake (Tylmann, 2005), which is responsible for the change of sediment texture in Yangzong Lake during 1985–1992 AD. During 1998–2002 AD, all the metals showed peak values except Ca, and more sand fractions ($> 63 \mu\text{m}$) were transported into Yangzong Lake, which may also be related to increased erosion. In addition, the extraordinary variations in Pb and Zn in the sediments of Yangzong Lake during 1985–1992 AD and 1998–2002 AD were accompanied by variations in the major metals. Lower normalized Pb and Zn (Pb/Al and Zn/Al) values until 2000 AD and higher values afterward, denote anthropogenic input in addition to the detrital origins.

Anthropogenic Pb from industrial waste, ore mining and smelting, coal burning, and leaded gasoline could significantly shift the Pb isotope ratios, which give more exact information about the source and timing of human pollution (Marx et al., 2010; Cheng and Hu, 2010; Balogh et al., 2010). $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ showed constant values before 1990 AD and then increased rapidly, implying that anthropogenic input of Pb and Zn did not dominate the accumulation in the sediments of Yangzong Lake before 1990 AD. This phenomenon is consistent with the result deduced from the variations of normalized values of Pb and Zn. In contrast to trace metal pollution in the western industrial countries (Yang and Rose, 2003, 2005; Nriagu, 1996), China started overall economic recovery in the 1950's after the end of the civil war in 1949, and

experienced the first stage of industrial and agricultural development in the 1970s and economic boom since the 1990's. Therefore, the pollution history of Pb and Zn in Yangzong Lake is consistent with the industrial development stages in Yunnan Province, and is also similar to the trace metal pollution history in Fuxian Lake in southwestern China (Zeng and Wu, 2009). The relatively early starting time of Pb pollution revealed by the isotope data compared to that observed in the concentration data also indicated that isotope ratios of lead could respond to the pollution more sensitively.

Anthropogenic Pb is mainly considered to arise from non-point sources such as atmospheric transport and precipitation resulting from the mining and smelting industry, coal burning, use of gasoline before the prohibition of leaded gasoline, and other industrial activities (Marx et al., 2010; Cheng and Hu, 2010; Balogh et al., 2010; Wu et al., 2004). Anthropogenic Pb of gasoline origin could significantly shift the Pb isotope ratios, thus isotopic fingerprinting can be used as a convenient tool to differentiate the inputs from the natural and anthropogenic Pb from gasoline use (Cheng and Hu, 2010). The phase-out of leaded gasoline in China started in the 1990s, with leaded gasoline being banned in several major cities, including Beijing, Shanghai and Tianjin, in 1997–1998, and a nationwide ban in 2000 (Cheng and Hu, 2010). $^{207}\text{Pb}/^{206}\text{Pb}$ in atmospheric aerosols in Shanghai and Tianjin decreased steadily with the phasing out of leaded gasoline use (Chen et al., 2005; Wang et al., 2006). In our study, $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ showed constant lower values before 1990 AD and then increased rapidly, but no decrease could be observed after around 2000 AD, which is contrary to the decreasing values of $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ from atmospheric deposition after the prohibition of using leaded gasoline in China since the 1990's (Cheng and Hu, 2010). Therefore, direct atmospheric deposition of Pb from the use of gasoline may not be mainly responsible for the pollution since the 1990's recorded in Yangzong Lake.

Trace metal pollution from atmospheric deposition due to coal burning has usually been accompanied by the massive deposition of SCPs in sediments (Yang and Rose, 2003, 2005). An abrupt increase in SCP concentrations at the depth of 20.5 cm was accompanied by the installation and start up of the Yangzong Power Plant in 1959 AD. SCPs maintained high values till 1985 AD. The lower concentrations of SCPs in 10.5–6.5 cm (1985–1992 AD) and 5–2.5 cm (1998–2002 AD) corresponded to the higher sedimentary rates. The decreasing SCP concentration in the upper 2.5 cm, where no increase in sedimentary rate could be found, may be related to the smoke pollution control of power plants in recent years. However, Pb and Zn showed no significant enrichment in the sediments with the increase in SCPs since the 1960's. $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ did not vary with the variations in SCPs concentrations. Therefore, it is concluded that atmospheric deposition from coal burning was not the dominant anthropogenic source for Pb and Zn in Yangzong Lake although its contribution cannot be negligible.

As one of the major non-ferrous production areas in

China, the non-ferrous production in Yunnan Province increased to about 1.5×10^5 tons annually by the mid-1980's from less than 1×10^4 tons in the early 1950's, and then reached over 2.0×10^6 tons in recent years. The isotope values of $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ in the Pb-Zn ore of Yunnan Province are significantly higher than those in the sediments of Yangzong Lake (Xue et al., 2007; Xu et al., 2010). Moreover, variations in $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios in the sediments of Yangzong Lake since 1990 AD tend towards their ranges in the Pb-Zn ores with the enhancement of nonferrous production (Xue et al., 2007; Xu et al., 2010). Therefore, we deduced that atmospheric deposition from Pb-Zn ore mining and refining, which typically causes Pb and Zn pollution (Xue et al., 2007), may contribute to the Pb and Zn pollution in Yangzong Lake.

5 Conclusions

All metals studied in the current investigation display significant variations in concentrations with depth. Principal component analysis allowed two main groups to be distinguished that are characterized by natural origins (PC1 and PC2, dominated by Al, Fe, Na, K, Ca, Ti, Mg and Li) and human input (PC3, Pb and Zn). Changes in terrestrial detrital material input to the lake due to human perturbations in the catchment have exerted influence on the concentrations of major and trace metals. A geochemical normalization technique allowed the removal of artifacts in the metal concentrations due to changes in sediment textures and anthropogenic input differentiation. Increasing values of normalized Pb and Zn, and $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ in the sediment denoted the anthropogenic input since around 1990 AD. The discrepancy between variations in $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios in the sediments of Yangzong Lake from the values in the airborne particles with the phase-out of leaded gasoline in China since the 1990's suggested that atmospheric deposition of Pb and Zn from vehicle emissions did not dominate the pollution in Yangzong Lake. The synchronous variations in $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$, and nonferrous production, and the convergence of $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ in the sediments to their values in Pb-Zn ores demonstrated that atmospheric input sourcing from ore mining and refining dominated the Pb and Zn pollution in Yangzong Lake.

Acknowledgments

This work was supported by the Nanjing Institute of Geography & Limnology, the Chinese Academy of Sciences (No. NIGLAS2011KXJ002), the National Basic Research Program (973) of China (No. 2010CB950201, 2012CB956104) and the National Natural Science Foundation of China (No. 40772204, 41072267). We are grateful to Dr. Zhijun Gong, Dr. Feizhou Chen and Dr. Guimin Liu for their help on fieldwork, to Mr. Yuxin Zhu and Mr. Weilan Xian for providing the chemical and chronology data.

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Journal of Environmental Sciences (Established in 1989)

Vol. 24 No. 7 2012

Supervised by	Chinese Academy of Sciences	Published by	Science Press, Beijing, China
Sponsored by	Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences		Elsevier Limited, The Netherlands
Edited by	Editorial Office of Journal of Environmental Sciences (JES) P. O. Box 2871, Beijing 100085, China Tel: 86-10-62920553; http://www.jesc.ac.cn E-mail: jesc@263.net , jesc@rcees.ac.cn	Distributed by	Domestic Science Press, 16 Donghuangchenggen North Street, Beijing 100717, China Local Post Offices through China Foreign Elsevier Limited http://www.elsevier.com/locate/jes
Editor-in-chief	Hongxiao Tang	Printed by	Beijing Beilin Printing House, 100083, China
CN 11-2629/X	Domestic postcode: 2-580		Domestic price per issue RMB ¥ 110.00

ISSN 1001-0742



9 771001 074123